Physiologia Plantarum 2018 ISSN 0031-9317

Variation in the angiosperm ionome

Konrad Neugebauer[a,b], Martin R. Broadley[b], Hamed A. El-Serehy[c], Timothy S. George[a], James W. McNicol[d], Milton F. Moraes[e] and Philip J. White[a,f,*]

[a]Ecological Science Group, The James Hutton Institute, Dundee DD2 5DA, UK
[b]Plant and Crop Sciences Division, University of Nottingham, Loughborough, LE12 5RD, UK
[c]Zoology Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[d]Biomathematics & Statistics Scotland, Dundee DD2 5DA, UK
[e]Graduate Program of Tropical Agriculture, Federal University of Mato Grosso, Barra do Garças, Mato Grosso, Brazil
[f]Distinguished Scientist Fellowship Program, King Saud University, Riyadh 11451, Saudi Arabia

Correspondence
*Corresponding author,
e-mail: philip.white@hutton.ac.uk

Received 10 October 2017;
revised 15 January 2018

doi:10.1111/ppl.12700

The ionome is defined as the elemental composition of a subcellular structure, cell, tissue, organ or organism. The subset of the ionome comprising mineral nutrients is termed the functional ionome. A 'standard functional ionome' of leaves of an 'average' angiosperm, defined as the nutrient composition of leaves when growth is not limited by mineral nutrients, is presented and can be used to compare the effects of environment and genetics on plant nutrition. The leaf ionome of a plant is influenced by interactions between its environment and genetics. Examples of the effects of the environment on the leaf ionome are presented and the consequences of nutrient deficiencies on the leaf ionome are described. The physiological reasons for (1) allometric relationships between leaf nitrogen and phosphorus concentrations and (2) linear relationships between leaf calcium and magnesium concentrations are explained. It is noted that strong phylogenetic effects on the mineral composition of leaves of angiosperm species are observed even when sampled from diverse environments. The evolutionary origins of traits including (1) the small calcium concentrations of Poales leaves, (2) the large magnesium concentrations of Caryophyllales leaves and (3) the large sulphur concentrations of Brassicales leaves are traced using phylogenetic relationships among angiosperm orders, families and genera. The rare evolution of hyperaccumulation of toxic elements in leaves of angiosperms is also described. Consequences of variation in the leaf ionome for ecology, mineral cycling in the environment, strategies for phytoremediation of contaminated land, sustainable agriculture and the nutrition of livestock and humans are discussed.

Introduction

The ionome is defined as the elemental composition of a subcellular structure, cell, tissue, organ or organism (Salt et al. 2008, White and Brown 2010). It includes all mineral elements, whether essential or non-essential for life, in whatever chemical form they occur. The ionome is influenced by both genetic and environmental factors. The ionome of a particular plant, organ, tissue, cell or subcellular structure is affected by the phytoavailability of elements in the environment, transport processes into and within the plant, plant metabolism and the requirements of specific extracellular and intracellular structures (White and Brown 2010, Baxter 2015). The ionome differs between plant species growing in the same environment (Broadley et al. 2004, White

Abbreviations – DM, dry matter; NFT, Nutrient Film Technique.

et al. 2012b, Watanabe et al. 2016), organs, tissues and cells of an individual plant (Sorreano 2006, Cakmak et al. 2010, Conn and Gilliham 2010, Subramanian et al. 2011, Baxter et al. 2012, Eggert and von Wirén 2013, Zhao et al. 2014, He et al. 2016, Persson et al. 2016, Thomas et al. 2016, Watanabe et al. 2016, de la Fuente et al. 2017, White and Pongrac 2017) and extracellular and intracellular compartments (Sterner and Elser 2002, Hawkesford et al. 2012, Broadley et al. 2012a, 2012b, White et al. 2018). Ultimately, differences in the ionomes of plants growing under identical conditions reflect differences in their genomes and gene expression that have evolved through mutation and the selection of adapted phenotypes. Variation in the ionome of plant species, and among genotypes of plant species, has profound consequences for ecology, mineral cycling in the environment, strategies for the phytoremediation of contaminated land, sustainable agriculture and the nutrition of livestock and humans.

Variation in the optimal ionome of individual plants has consequences for ecological strategies and species survival. Since the optimal ionome for the growth and fecundity of a plant is related to (1) its requirements for mineral nutrients, (2) its retention of mineral nutrients, (3) its tolerance to non-essential elements and (4) the availability of these elements in its environment, genetic effects on the optimal ionome can influence responses of plant communities to environmental change (Willby et al. 2001, Crawley et al. 2005, Semelova et al. 2008, Elser et al. 2010, Hejcman et al. 2010, 2014, Grime and Pierce 2012, Hayes et al. 2014, Sardans et al. 2015, Kidd et al. 2017). Aspects of the shoot ionome are correlated with various ecological traits, including leaf mass per unit area, stress-tolerance, photosynthetic metabolism, monopolisation of resources and relative growth rates (Thompson et al. 1997, Grime 2001, Sterner and Elser 2002, Fyllas et al. 2009, Saslis-Lagoudakis et al. 2014, Viani et al. 2014, Carnicer et al. 2015). The ability (1) to exclude potentially toxic elements from the plant or to sequester them in specialised cell types or subcellular compartments to avoid toxicity, and (2) to accumulate ions that form salts of low solubility in different cell types or cellular compartments, allows plants to grow on hostile soils or soils with imbalanced nutrient availability (Conn and Gilliham 2010, Flowers et al. 2015, White 2016a, Lange et al. 2017, Schiavon and Pilon-Smits 2017, White and Pongrac 2017). In addition, the ability to accumulate large concentrations of potentially toxic elements can provide a deterrent to pathogens and herbivores, and confer allelopathy (Schiavon and Pilon-Smits 2017, White and Pongrac 2017). Knowledge of the plant species or genotypes of a species that accumulate potentially toxic elements (Dhillon and Bañuelos 2017, White and Pongrac 2017) or radionuclides (White et al. 2003, Willey 2014, Penrose et al. 2016) can inform contaminant transfer models (Beresford et al. 2004, Willey 2014) and the choice of species for use or phytoremediation of contaminated land (Reeves 2006, Rozema and Schat 2013, Willey 2014, Dhillon and Bañuelos 2017, Lange et al. 2017, White and Pongrac 2017).

Phylogenetic variation in the optimal ionome among plant species influences the accumulation of mineral elements from soils, their distribution between plant tissues, and their cycling in the soil-plant-herbivore-environment continuum (White et al. 2013b). This has consequences for optimising agricultural systems, e.g. in the return of mineral elements from crop remains to soil (Defra 2010), designing intercropping and rotations that optimise fertiliser applications (Brooker et al. 2015), and producing nutritionally balanced food, feed and forage (White and Broadley 2009, Watson et al. 2012, White 2016b). Crop production is often restricted by insufficient nitrogen (N), phosphorus (P) and potassium (K) supply (Fageria et al. 2011, Mueller et al. 2012), and by adverse soil conditions, such as acidity and alkalinity, salinity, sodicity, soil compaction and water availability that affect the phytoavailability of mineral nutrients (White et al. 2013a, 2013b, Jin et al. 2017). Genetic variation between and within plant species in their nutrient requirements can be exploited to develop crops for adverse soil conditions and restricted nutrient availability (Fageria et al. 2011, Veneklaas et al. 2012, Yang et al. 2012, White et al. 2012a, White 2013). Differences in the mineral composition of plant species, which are the foundation of food chains, and tissues within plants also have important consequences for the diets of herbivores and omnivores (White and Broadley 2009, Watson et al. 2012, Schonewille 2013, White et al. 2013b, White 2016b) and affect their development, health and fecundity. Variation in the ionome of plants, which influences the mineral composition of forage, feed and food, will affect the ecology of natural communities and the health of farmed animals and humans. Ill heath in livestock can often result from insufficient or imbalanced K, sodium (Na), calcium (Ca), magnesium (Mg), P, selenium (Se) or iodine (I) intakes, and managing the species composition and forage quality of grasslands and the development of plants with better mineral composition for forage and feed are high on the agenda (White and Broadley 2009, Watson et al. 2012, Knowles and Grace 2013, Dove et al. 2016). In parallel, since most mineral nutrients in human diets are provided either directly or indirectly by edible plants, variation in the mineral composition of edible produce is of considerable importance for human nutrition (White and Broadley 2009, Saltzman et al. 2013, White et al. 2013b, White 2016b). Thus,

agronomic strategies, such as the use of fertilisers and soil amendments, in combination with efforts to identify crops and breed cultivars with greater mineral densities in their edible portions are being actively pursued (White and Broadley 2009, Saltzman et al. 2013, White 2016b).

In this article, environmental and phylogenetic effects on mineral composition of flowering plants (angiosperms) will be illustrated using the ionome of leaves. The concept of a 'functional ionome', comprising only the essential mineral nutrients for plant growth, will be introduced, the effects of the soil environment on the ionome of leaves will be described, and the evolution of particular ionomic traits will be presented.

The functional ionome

The functional ionome comprises the 14 mineral nutrients required by plants: N, P, K, Ca, Mg, sulphur (S), chlorine (Cl), boron (B), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni) and molybdenum (Mo). Each of these elements has unique functions and, consequently, cannot be replaced by any other element (Hawkesford et al. 2012, Broadley et al. 2012a, Grusak et al. 2016).

A 'standard functional ionome' of leaves of angiosperms can be defined as their nutrient composition when plant growth is not limited by mineral nutrients. This standard functional leaf ionome can be determined from surveys of the leaf ionomes of a representative selection of angiosperms grown under nutrient-replete conditions. This might be achieved by sampling species from their natural habitats (Reich and Oleksyn 2004, Watanabe et al. 2007, Fyllas et al. 2009, Zhang et al. 2012, White et al. 2012b, Cornwell et al. 2014, Hao et al. 2014, Hayes et al. 2014, Sardans et al. 2015, He et al. 2016, Verboom et al. 2017) or by growing species in controlled environments (Broadley et al. 2003, 2004, White et al. 2007, 2017). Each of these approaches offers advantages and disadvantages. It is almost certain that plant species are adapted to obtain their nutrient requirements from the environments in which they grow (White et al. 2013a, 2013b, Hayes et al. 2014, Lambers et al. 2015, Oliveira et al. 2015, Verboom et al. 2017, White and Pongrac 2017). Sampling plants from their natural habitats allows the effects of adaptive traits on the leaf ionome to be expressed and interactions with native biota to exist, but the effects of the environment on both plant growth and on the absolute and relative phytoavailability of mineral elements are maximised. In addition, the requirement that growth should not be limited by mineral nutrition is often compromised when plants are sampled from the natural environment (Ostertag and DiManno 2016). Growing plants under controlled conditions reduces environmental effects but the choice of experimental system, substrate and nutrient supply is challenging. The growth of plants specialised to particular environments can be compromised due to lack or excess of mineral elements. For example, the P supply required for optimal growth of most plants can be toxic to plants adapted to soils with low P phytoavailability, such as the Proteaceae (Lambers et al. 2015), calcicole and calcifuge species require markedly different Ca supply for optimal growth (White and Broadley 2003), the growth of plants that hyperaccumulate nutrients is often reduced when they are supplied in amounts that are sufficient for most other plants (White and Pongrac 2017), and the maximal growth of euhalophyte species requires a Na supply that inhibits the growth of other plant species (Greenway and Munns 1980, White et al. 2017). Growing plants in a standard soil or potting medium allows naturalistic interactions between roots and soil to be expressed, such as the exudation of organic compounds including phytosiderophores and carboxylates, acidification of the rhizosphere and formation of rhizosheaths, but can also constrain these interactions by influencing root-soil interactions and the phytoavailability of nutrients and toxic elements (Delhaize et al. 2012, White 2012, Oliveira et al. 2015, Brown et al. 2017) and promote interactions with a predetermined community of microorganisms. Growing plants hydroponically allows the phytoavailability of nutrients to be controlled, but restricts the expression of physico-chemical interactions between the root and rhizosphere and the composition of the nutrient solution (and plant species) must be chosen wisely to ensure that plant growth is not constrained by nutrient supply.

In principle, species used to define the standard functional leaf ionome should be selected randomly, pro rata to the phylogenetic distribution of all angiosperm species (Broadley et al. 2003). However, this is often not possible in practice because (1) plants must be grown under the same conditions, and some plants might not germinate or survive these conditions, which compromises random selection, and (2) some orders contain few species, which necessitates growing an impossibly large number of species to achieve pro rata sampling. However, it has been observed that unbalanced data generally yield comparable information to phylogenetically balanced experiments (Broadley et al. 2003, White et al. 2012b).

Data for the functional ionomes of leaves of 334 angiosperm species representing 79 families and 35 orders (Table S1) were obtained from the six glasshouse experiments described by White et al. (2017), which incorporated the studies of Broadley et al. (2004) and

White et al. (2007, 2015). In these experiments plants were grown hydroponically using the Nutrient Film Technique (NFT) described by Broadley et al. (2003). The composition of the nutrient solution was 2 mM $Ca(NO_3)_2$, 2 mM NH_4NO_3, 0.75 mM $MgSO_4$, 0.5 mM KOH, 0.25 mM KH_2PO_4, 0.1 mM FeNaEDTA, 30 μM H_3BO_3, 25 μM $CaCl_2$, 10 μM $MnSO_4$, 3 μM $CuSO_4$, 1 μM $ZnSO_4$ and 0.5 μM Na_2MoO_4, adjusted to pH 6 with H_2SO_4. Seedlings were harvested during the exponential growth phase, 18–73 days after transfer to the hydroponic system, depending on the plant growth rate, and mineral concentrations in leaves were determined using standard analytical techniques (White et al. 2017).

The standard functional leaf ionome was calculated from these data as the weighted (by number of species in an order) mean of the average leaf ionome of the angiosperm orders sampled. The number of species in each order was obtained from the Angiosperm Phylogeny website (Stevens 2001). The leaf ionome of a particular species was calculated as the mean value for each mineral nutrient across all experiments in which the species was grown. The average leaf ionome of a plant order was calculated as the mean value for each mineral nutrient of the species sampled in that order across all six experiments. The value of each element in the standard functional leaf ionome was calculated as the sum, for all the orders sampled, of its value in the average leaf ionome of an order multiplied by the number of species in that order, divided by the sum of the number of species in all orders sampled. The standard functional leaf ionome comprised (mg g^{-1} leaf dry matter): 50.4 N, 39.7 K, 39.4 organic N, 13.6 Ca, 7.22 P, 4.24 Cl, 3.92 S, 3.61 Mg, 1.26 Na, 0.181 Mn, 0.144 Fe, 0.0745 Zn, 0.0412 B, 0.0141 Cu, 0.0014 Ni. This can be compared with the simple mean of the angiosperm orders sampled (the value for each order being calculated as the mean of the species within that order, Table S1) which comprised (mg g^{-1} leaf dry matter, mean ± SE, n orders): 51.3 ± 2.03 (n = 28) N, 36.3 ± 2.63 (n = 35) K, 38.0 ± 1.83 (n = 32) organic N, 15.4 ± 1.92 (n = 35) Ca, 6.88 ± 0.35 (n = 35) P, 5.28 ± 0.52 (n = 17) Cl, 5.08 ± 0.40 (n = 20) S, 3.83 ± 0.20 (n = 35) Mg, 1.12 ± 0.17 (n = 35) Na, 0.233 ± 0.037 (n = 32) Mn, 0.171 ± 0.013 (n = 24) Fe, 0.0176 ± 0.0019 (n = 22) Cu, 0.1032 ± 0.0123 (n = 24) Zn, 0.0555 ± 0.0058 (n = 24) B and 0.0016 ± 0.0002 (n = 17) Ni. These values can be compared with estimates of the critical leaf concentrations of these elements for sufficiency, defined as the concentration in a diagnostic leaf tissue that allows a crop to achieve 90% of its potential yield, and toxicity, defined as the concentration in a diagnostic leaf tissue above which potential yield is reduced by more than 10% (White and Brown 2010). It can be observed that the standard functional leaf ionome calculated from the studies described by White et al. (2017) lies within the bounds of sufficiency and toxicity for all nutrients. The standard functional leaf ionome is, therefore, representative of the leaves of the 'average' angiosperm when plant growth is not limited by mineral nutrients and can be used to facilitate comparisons of plant taxa and environmental conditions.

Relationships between individual mineral elements in the leaf ionome

Correlations exist between leaf concentrations of individual nutrients among plant species when their growth is not limited by mineral nutrition. The two relationships most commonly observed are (1) an allometric relationship between leaf P concentration and leaf N concentration, with leaf N scaling either as the two-thirds or three-quarters power of leaf P concentration in herbaceous plants (Fig. 1A; Garten 1976, Thompson et al. 1997, Sterner and Elser 2002, Broadley et al. 2004, Wright et al. 2004, Kerkhoff et al. 2006, Niklas 2006, Fyllas et al. 2009, Elser et al. 2010, Reich et al. 2010, Veneklaas et al. 2012) and (2) linear relationships between leaf Ca concentration and leaf Mg concentration among specific groups of angiosperms (Fig. 1B, C; Garten 1976, Thompson et al. 1997, Broadley et al. 2004, Watanabe et al. 2007, Fyllas et al. 2009, White 2012, White et al. 2015, 2018, Hao et al. 2014, Verboom et al. 2017).

In the absence of 'luxury' N or P accumulation, the organic-N:P concentrations of leaves often approximate 6:1 on a g N:g P basis (Fig. 1A; Broadley et al. 2004), which is similar to the maximum critical organic-N: critical P concentration ratio determined for a range of crop species (Greenwood et al. 1980) and is consistent with a protein:RNA ratio of about 15 (assuming ratios of ester-P: nucleic acid P:lipid-P:inorganic-P of 1:2:1.3:1.4, Veneklaas et al. 2012). Differences in foliar N:P ratios of plants with balanced growth are generally related to differences in leaf P concentrations, rather than leaf N concentrations (Sterner and Elser 2002, Raven 2015). Since growth rates of organisms are positively correlated with rRNA abundance, greater foliar P concentrations are generally associated with greater growth rates and, through this, ecological strategy (Sterner and Elser 2002, Niklas 2006, Raven 2015). In general, when plant growth is limited by N supply foliar N/P quotients are <4–19, whereas when plant growth is limited by P supply foliar N/P quotients are >9–20 (Koerselman and Meuleman 1996, Güsewell 2004, Ostertag and DiManno 2016). Optimal foliar N/P quotients vary with plant species, growth rate and plant age (Güsewell 2004, Lambers

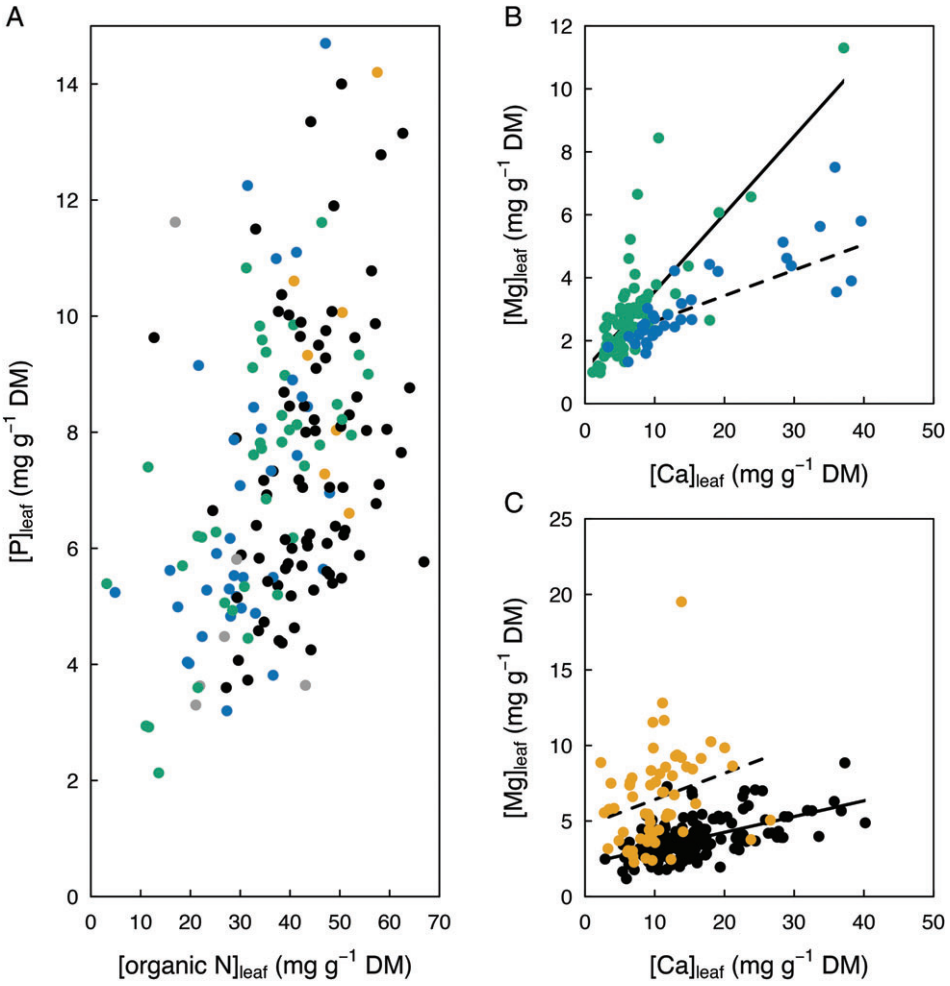

Fig. 1. Correlations between (A) leaf phosphorus ($[P]_{leaf}$) and leaf organic nitrogen concentrations ($[organic\ N]_{leaf}$) among 166 angiosperm species and leaf magnesium ($[Mg]_{leaf}$) and leaf calcium ($[Ca]_{leaf}$) concentrations in (B) commelinid monocots (green, 76 species), non-commelinid monocots (blue, 35 species) and (C) Caryophyllales (orange, 61 species) and other eudicots (black, 151 species). The regression lines in (B) and (C) are $[Mg]_{leaf} = 1.09 + 0.25\ [Ca]_{leaf}$ for commelinid monocots, $[Mg]_{leaf} = 1.40 + 0.11\ [Ca]_{leaf}$ for non-commelinoid monocots, $[Mg]_{leaf} = 4.68 + 0.17\ [Ca]_{leaf}$ for Caryophyllales and $[Mg]_{leaf} = 2.17 + 0.10\ [Ca]_{leaf}$ for other eudicots. Data are mean values for individual species represented in the experiments described by White et al. (2017) and listed in Table S1. The original data set included six basal angiosperms and magnoliids (grey) that are only plotted in (A) and three non-commelinid species with $[Ca]_{leaf} > 50\ mg\ g^{-1}$ dry matter that are not plotted in (B).

et al. 2015, Ostertag and DiManno 2016, Verboom et al. 2017).

It has been argued that distinct linear relationships between leaf Ca concentration and leaf Mg concentration are exhibited by commelinid monocots, non-commelinid monocots, eudicots excluding Caryophyllales and Caryophyllales species (Fig. 1B, C; White et al. 2018). The gradients of these relationships appear to be determined by cell wall chemistry and the Mg/Ca mass quotients in cell walls of the different groups of species (White et al. 2018). Differences in leaf Mg concentration and leaf Ca concentration between species within each group can be attributed to differences in the cation exchange capacity of their cell walls (White and Broadley 2003, White et al. 2018). The relatively large leaf Mg concentrations of Caryophyllales species have been attributed to their ability to accumulate more Mg in their vacuoles than other species when grown without a supra-sufficient Mg supply (White et al. 2015). Strong correlations between leaf Ca concentrations and leaf strontium (Sr) concentrations are also commonly observed among angiosperm species (White 2001, Watanabe et al. 2007, Broadley and White 2012), whilst correlations between leaf Ca concentrations and leaf barium (Ba) concentrations are sometimes, but not always, weak (White 2001, Watanabe et al. 2007). Leaf

concentrations of silicon (Si), which is designated as a beneficial element for plants, appear to be inversely related to leaf concentrations of Ca and Mg among angiosperms (Hodson et al. 2005). In general, leaf concentrations of Ca, Mg, Ba and Sr decrease, and leaf Si concentrations increase, in the order commelinid monocots, non-commelinid monocots and eudicots.

Strong positive correlations between leaf concentrations of mineral micronutrients also occur among angiosperm species. For example, Broadley et al. (2001) observed strong correlations between leaf Zn, Cu and Ni concentrations among angiosperms, suggesting that traits have evolved that impact on leaf concentrations of all these elements simultaneously. In addition, Broadley et al. (2001) observed that leaf Zn concentrations were correlated with leaf cadmium (Cd) concentrations, leaf Ni concentrations were correlated with leaf Cd and chromium (Cr) concentrations, and leaf Cu concentrations were correlated with leaf Cd, Cr and lead (Pb) concentrations. The elements Cd, Cr and Pb are not nutrients and are potentially harmful to plants and other organisms (White and Brown 2010, White et al. 2012a).

Effects of the environment on the leaf ionome

The environment in which a plant grows can have a profound effect on its ionome, by influencing (1) plant growth and development and (2) the relative phytoavailability of mineral elements, both directly and indirectly. In addition to soils with innate mineral imbalances, soil pH has a major effect on the phytoavailability of mineral nutrients and the flora of a location (Crawley et al. 2005, Hejcman et al. 2010, 2014, Viani et al. 2014, Kidd et al. 2017). Alkaline and calcareous soils reduce the phytoavailability of P, Fe, Zn, Mn and Cu whilst acid soils reduce the phytoavailability of P, Mo, Mg, Ca and K and raise concentrations of aluminium (Al) and Mn, both of which can be toxic to plants (White et al. 2013a, White and Pongrac 2017). Plants have adapted to infertile soils through efficient nutrient acquisition or utilisation (Fageria 2009, Veneklaas et al. 2012, White 2013, White et al. 2013a, 2013b, Hayes et al. 2014, Lambers et al. 2015, Oliveira et al. 2015, Verboom et al. 2017) and to hostile soils by excluding potentially toxic elements or by developing greater tolerance to their presence in tissues (Flowers et al. 2015, White 2016a, White and Pongrac 2017). Thus, significant (phylo)genetic and environment interactions occur among plant species in their abilities to acquire and accumulate mineral elements, which are driven by constant adaptation to their environment and survival (White and Broadley 2003, Sardans et al. 2015, White and Pongrac 2017).

Factors that affect soil structure or soil water content, such as drought, waterlogging or low temperatures, influence the phytoavailability of mineral nutrients indirectly. Both drought and low temperatures can reduce (1) the uptake of nutrients from the soil, and plant growth through plant nutrition, and (2) plant growth independently of nutrient supply. The effects of these stresses on the leaf ionome can be complex. For example, in cherry tomatoes the effects of drought on the leaf ionome differs between cultivars (Sánchez-Rodríguez et al. 2010). In 'Kosako' leaf concentrations of N, Cu, Mn, Zn, Cl and B were reduced by drought, whereas in 'Zarina' leaf concentrations of many elements were increased and only the concentrations of S and Mn were reduced. This observation implies that drought stress does not have a unique ionomic 'signature'.

In addition to affecting plant growth, development and anatomy (Hawkesford et al. 2012, Broadley et al. 2012a, Baxter 2015), the lack of a particular mineral nutrient often changes the concentrations of other mineral elements as a consequence of reduced interactions between elements for uptake by roots (White 2012), compensatory responses in the regulation of non-selective acquisition and transport processes (Hawkesford et al. 2012, Broadley et al. 2012a, Baxter 2015, Maillard et al. 2016), changes in metabolism (Hermans et al. 2006, White 2012, 2016a), obligate biochemical stoichiometries (Maillard et al. 2016), or altered electrochemical or osmotic gradients (White 2013). In general, when growth is limited by a particular nutrient, plants accumulate elements supplied in excess of requirements (Sterner and Elser 2002, Hawkesford et al. 2012, Broadley et al. 2012a, 2012b). The effects of nutrient deficiencies on the ionomes of many plant species have been documented (Sorreano 2006, Baxter et al. 2008, Parent et al. 2013b, Tomasi et al. 2014, Pii et al. 2015, Watanabe et al. 2015, Maillard et al. 2016, Campos et al. 2017). It has been proposed that alterations in the ionome might be used to diagnose particular physiological conditions, such as mineral deficiencies, much more accurately than assays of single elements (Baxter et al. 2008, Parent et al. 2013a, 2013b, Pii et al. 2015, Campos et al. 2017), but it has yet to be proven that the ionomes of all angiosperms respond similarly to nutrient deficiencies. In the native Brazilian plant *Cariniana legalis* (Mart.) Kuntze (Lecythidaceae), the consequences of deficiencies of individual mineral nutrients on the shoot ionome are quite distinct (Fig. 2; Sorreano 2006). Magnesium deficiency reduced shoot concentrations of Fe, B and Ca and increased shoot Mo concentration (Fig. 2A). Similarly, Ca deficiency reduced shoot concentrations of Fe and B and increased shoot Mo, K and S concentrations (Fig. 2A) and K deficiency

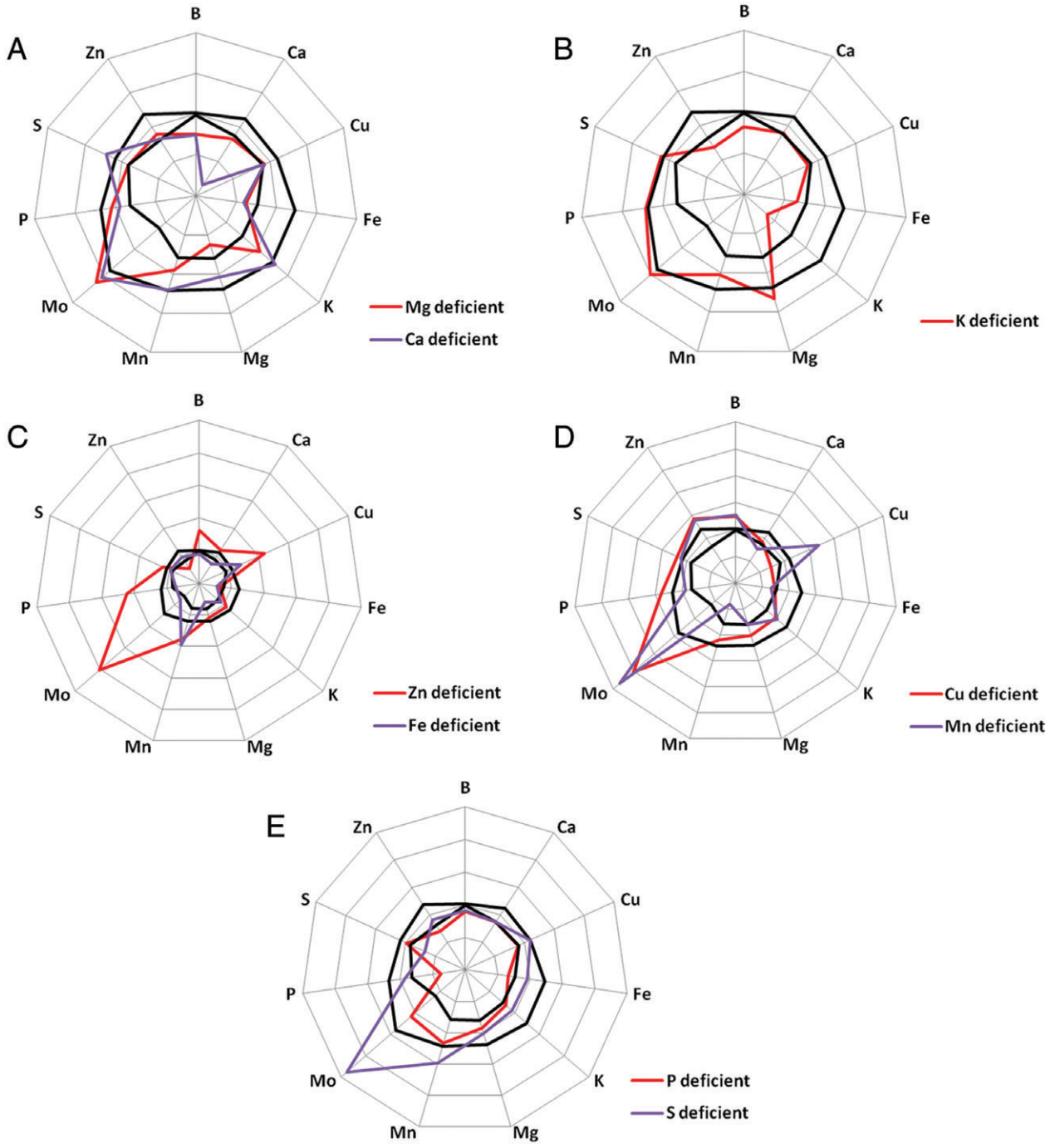

Fig. 2. The effects of mineral deficiencies on the functional ionome of shoots of the native Brazilian plant *Cariniana legalis* (Mart.) Kuntze (Lecythidaceae). Data are scaled to the means of three biological replicates obtained in nutrient replete conditions, which were: Boron (B) 58.4 $\mu g\, g^{-1}$ DM, calcium (Ca) 24.1 $mg\, g^{-1}$ DM, copper (Cu) 2.35 $\mu g\, g^{-1}$ DM, iron (Fe) 426 $\mu g\, g^{-1}$ DM, potassium (K) 18.9 $mg\, g^{-1}$ DM, magnesium (Mg) 4.67 $mg\, g^{-1}$ DM, manganese (Mn) 38.7 $\mu g\, g^{-1}$ DM, molybdenum (Mo) 1.15 $\mu g\, g^{-1}$ DM, phosphorus (P) 4.57 $mg\, g^{-1}$ DM, sulphur (S) 2.90 $mg\, g^{-1}$ DM and zinc (Zn) 23.8 $\mu g\, g^{-1}$ DM. The shoot concentration of nitrogen was 22.7 $mg\, g^{-1}$ DM in nutrient replete conditions. Red and purple outlines indicate the concentrations of mineral nutrients obtained when the individual nutrients indicated were insufficient for plant growth. Black outlines represent differences of two standard errors from the mean value for each element obtained when plants were grown in nutrient replete conditions. Shoot concentrations of mineral elements were calculated from the data presented by Sorreano (2006).

reduced shoot concentrations of Fe, B, Cu and Zn and increased shoot Mo, Mg, P and S concentrations (Fig. 2B). Zinc deficiency had a profound effect on the shoot ionome, increasing concentrations of Ca, Cu, Mn, Mo, P, B and S and reducing Fe concentration (Fig. 2C). Similarly, Cu deficiency increased shoot concentrations of Zn, Mo, P, B and S and decreased shoot Fe concentration, whilst Mn deficiency increased shoot concentrations of Zn, Cu, Mo, B and S and decreased shoot Fe and Ca concentrations (Fig. 2D). Iron deficiency had less of an effect on the ionome, increasing shoot concentrations of Cu and Mn and reducing shoot concentrations of Ca, Mg, B and P (Fig. 2C). In general, anion deficiencies had less impact on the shoot ionome than cation deficiencies. Phosphorus deficiency resulted in reduced concentrations of B, Zn and Fe, whereas S deficiency resulted in a reduced shoot B concentration and increased Mn and Mo concentrations (Fig. 2E). The effects of N, B and Mo deficiencies on the shoot ionome were not studied in the experiments of Sorreano (2006).

Phylogenetic effects on the leaf ionome

In general, plant species from the same family grown in the same environment have similar leaf ionomes, whereas those of different families and orders are distinct (Broadley et al. 2004, White et al. 2012b). Furthermore, despite the effects of environment on the leaf ionome, strong phylogenetic effects on the mineral composition of plant species can still be observed even in extensive field surveys (Garten 1978, Thompson et al. 1997, Kerkhoff et al. 2006, Watanabe et al. 2007, Fyllas et al. 2009, Metali et al. 2012, Zhang et al. 2012, Cornwell et al. 2014, Hao et al. 2014, Viani et al. 2014, Sardans et al. 2015, He et al. 2016, Verboom et al. 2017), surveys of plots receiving contrasting fertilisation, such as the Rothamsted Park Grass Experiment (White et al. 2012b), and pot experiments with contrasting soils (Viani et al. 2011, Quintero-Vallejo et al. 2015). For example, the leaves of Poales are characterised by relatively small Ca, Mg and B concentrations, leaves of Brassicales are characterised by relatively large Ca, Zn and S concentrations, and leaves of Caryophyllales are characterised by relatively large Mg, Zn and Na concentrations (Fig. 1; Broadley et al. 2003, 2004, Osaki et al. 2003, Willey and Wilkins 2006, Watanabe et al. 2007, White et al. 2012b, 2015, 2017, He et al. 2016, Verboom et al. 2017). The most informative elements for discrimination between plant families or orders are generally Ca and Mg and the least informative N and P (White et al. 2012b, Parent et al. 2013a, 2013b). Similarly, when the genetic variation in element concentrations in leaves of angiosperm species is partitioned into a taxonomic hierarchy, it is often observed that the proportion of variation in leaf mineral concentration assigned to the order level and above is greater for Al, Ca, Mg and Si than for N and P (Thompson et al. 1997, Broadley et al. 2004, Hodson et al. 2005, Watanabe et al. 2007, Fyllas et al. 2009), which suggests that leaf concentrations of structural elements, such as Ca, Mg and Si, were influenced greatly by ancient evolutionary processes, whereas the concentrations of elements involved in metabolism, such as N and P, were subject to more recent evolutionary pressures.

Many studies have indicated differences between angiosperm orders in their leaf ionomes (Broadley et al. 2001, 2003, 2004, Osaki et al. 2003, Willey and Fawcett 2005, Willey and Wilkins 2006, Watanabe et al. 2007, White et al. 2012b, 2015, 2017). The evolution of differences in leaf concentrations of individual elements between plant species can be traced using phylogenetic relationships among angiosperm orders, families, genera and ecotypes (White et al. 2015, 2017, White 2016a, White and Pongrac 2017). Early studies indicated that commelinid monocots had smaller leaf Ca concentrations than other angiosperm species (Broadley et al. 2003, White et al. 2015). Consistent with these observations, the data set compiled from the experiments described by White et al. (2017) suggest that this trait is not present in the basal angiosperms or magnoliids [Fig. 3; Mean ± SE, n species: Piperales 14.63 ± 9.01 mg Ca g^{-1} dry matter (DM), n = 2; Laurales 7.56 ± 2.52 mg Ca g^{-1} DM, n = 2; Magnoliales 14.75 ± 0.15 mg Ca g^{-1} DM, n = 2] and that species from the earliest non-commelinid monocot orders to diverge, the Alismatales and Dioscoreales, exhibit conspicuously large leaf Ca concentrations (Fig. 4). The mean leaf Ca concentrations of families in the Liliales (12.84 mg Ca g^{-1} DM) and Asparagales (13.38 mg Ca g^{-1} DM) orders were less than those of other non-commelinid monocot orders and comparable to the mean leaf Ca concentrations of the basal angiosperms and magnoliids and to the commelinid monocot orders Arecales, Commelinales and Zingiberales (Fig. 4). Furthermore, the mean leaf Ca concentrations in all these clades were similar to that of the single species sampled from the Bromeliaceae, the earliest family to diverge within the Poales (Fig. 4). Indeed, small leaf Ca concentrations were only apparent in the Cyperaceae, Juncaceae and Poaceae, suggesting that the trait evolved within the Poales (Fig. 4). Since the trait is correlated to cell wall cation exchange capacity, which is largely determined by pectins, it was suggested that it was a consequence of the evolutionary shift from the type I cell walls of eudicots, in which the microfibrils are tethered together by xyloglucans and this framework

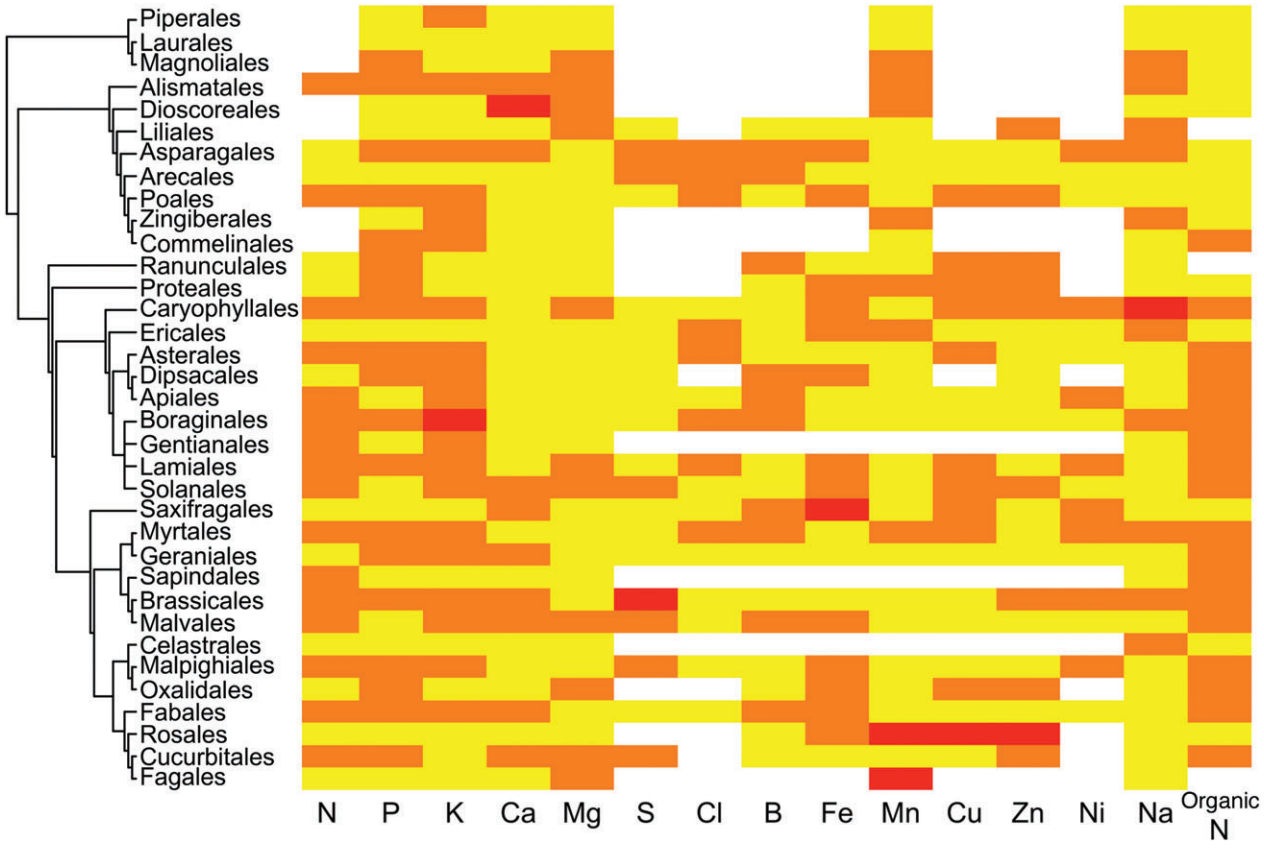

Fig. 3. Representation of the average ionomes of leaves of angiosperm orders calculated using data from the experiments described by White et al. (2017) as the mean value for each mineral nutrient of the species sampled in an order. The colour coding (yellow = small, orange = intermediate, red = large) is based on scaling the concentrations for each element across the orders sampled to have a mean of 0 and a SD of 1. Values coded yellow are less than −0.05 SD from the mean and values coded red are greater than 2.5 SD from the mean. Original data are presented in Table S1.

is embedded in a gel of pectins, to the type II walls of Poales, in which microfibrils are tethered with sugars such as glucuronoarabinoxylan and contain less xyloglucan and pectin (White and Broadley 2003). Commelinid monocots also have smaller leaf Mg concentrations than other angiosperms and this has been attributed to the same structural origin (Fig. 1; White et al. 2018). By contrast, members of the Caryophyllales order generally have larger leaf Mg concentrations than other angiosperm species (White et al. 2015). This trait does not appear in any other superasterid order, but was present in all the Caryophyllales families studied, suggesting that it arose in an ancient ancestor of all the Caryophyllales families (White et al. 2015). Members of the Brassicales order are characterised by relatively large leaf Ca and S concentrations (Fig. 3). Large leaf S concentrations were exhibited by species in all the Brassicales genera studied, with the exception of *Cardamine* (Fig. 5), and by one of the two Malvales species studied, but not by any of the three Myrtales or Geraniales species studied, suggesting that the trait arose when the Brassicales and Malvales separated from other malvid orders. The ability of Brassicales species to accumulate S has been attributed to their unique ability to synthesise glucosinolates (Ernst 1998). This ability is shared by most Brassicales genera, including *Cardamine*, but it is not present in Malvales or Sapindales species (Ronse de Craene and Haston 2006, Olsen et al. 2016).

The hyperaccumulation of mineral elements has been studied extensively (Reeves 2006, Broadley et al. 2007, Krämer 2010, Van der Ent et al. 2013, Cappa and Pilon-Smits 2014, White 2016a, White and Pongrac 2017). Hyperaccumulation has been defined as a concentration of a mineral element in shoot DM of a plant sampled from its natural environment greater than a set threshold concentration. Threshold concentrations for classifying hyperaccumulation are: 10 mg g^{-1} DM for Mn, 3 mg g^{-1} DM for Zn, 1 mg g^{-1} DM for Ni, Pb and Se, 0.3 mg g^{-1} DM for Co, Cr and Cu and 0.1 mg g^{-1} DM for Cd (White 2016a, White and Pongrac 2017).

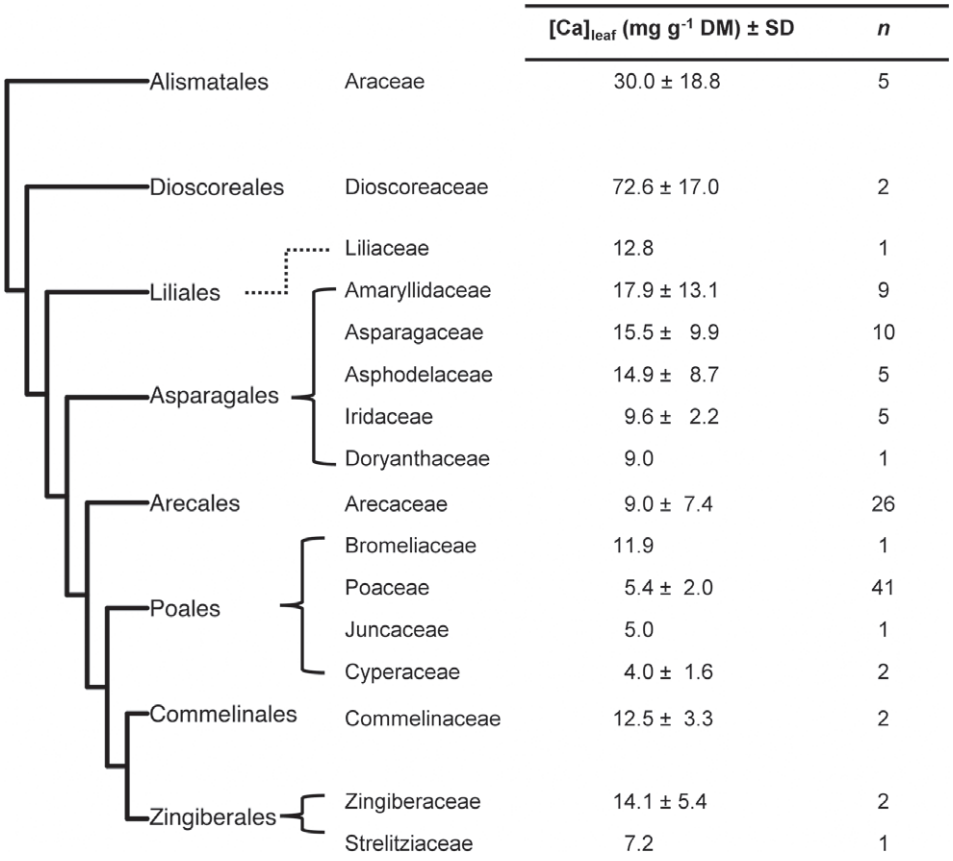

Fig. 4. Phylogenetic relationships between eight monocot orders according to the angiosperm phylogeny group (APG IV 2016). Mean leaf calcium concentrations of families within each order are expressed as means ± SD from the number of species stated. Data for individual species are mean values from the experiments described by White et al. (2017). Original data are presented in Table S1.

These values are greater than the concentrations that would be toxic to most plants (White and Pongrac 2017). The trait of hyperaccumulation is rare and occurs in less than 0.2% of all angiosperm species (Broadley et al. 2001, Reeves 2006, Krämer 2010, Van der Ent et al. 2013, Cappa and Pilon-Smits 2014, White 2016a, Lange et al. 2017, White and Pongrac 2017). The occurrence of Ni hyperaccumulation among angiosperms (400–450 species; 42 families) appears to be more frequent than that of Se hyperaccumulation (44 species; 6 families), Cu hyperaccumulation (30–35 species; 22 families), Co hyperaccumulation (25–30 species; 12 families), Mn hyperaccumulation (12–26 species; 6–9 families) or Zn hyperaccumulation (12–20 species; 4–6 families). The occurrence of Pb hyperaccumulation (14 species; 7 families), Cr-hyperaccumulation (11 species; 7 families) or Cd hyperaccumulation (2–7 species; <5 families) is relatively infrequent.

Although the ability to hyperaccumulate a particular mineral element evolved independently in many angiosperm clades, it is particularly prevalent in the Malpighiales, Brassicales, Asterales and Lamiales (White and Pongrac 2017). This has facilitated comparative studies on the physiology and evolution of the hyperaccumulation of mineral elements. The traits of Ni, Zn and Cd hyperaccumulation have been studied intensively in the Brassicaceae and it is believed that these traits evolved independently several times within this family. One evolutionary origin of both Ni hyperaccumulation and Zn hyperaccumulation occurs at the base of the *Raparia/Noccaea* clade and it has been speculated that Zn hyperaccumulation might be a modification of the Ni hyperaccumulation trait, but species that hyperaccumulate Zn do not always hyperaccumulate Ni (Broadley et al. 2007, Krämer 2010, Koch and German 2013). Similarly, Cd hyperaccumulation often occurs in Brassicaceae exhibiting Zn hyperaccumulation, such as *Noccaea* spp. and *Arabidopsis halleri*, though not in all populations of these species (Krämer 2010, Koch and German 2013, Sterckeman et al. 2017). By contrast, the ability to hyperaccumulate Cu or Co is most frequently observed in the Lamiales (Lange et al. 2017,

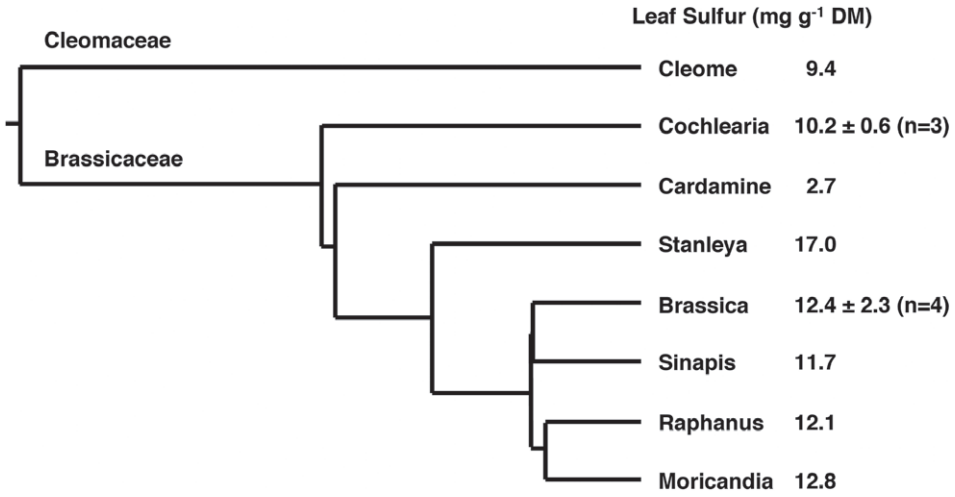

Fig. 5. Phylogenetic relationships, based on evolutionary time (Kumar et al. 2017) between eight genera of the Brassicales order, including species in the Cleomaceae and Brassicaceae families. The Cleomaceae and Brassicaceae are estimated to have diverged 46 MYA. Mean leaf sulphur concentrations of the *Cochlearea* and *Brassica* genera are expressed as means ± SE of three and four species, respectively. Other genera are represented by single species. Data for each species are mean values from the experiments described by White et al. (2017). Original data are presented in Table S1.

White and Pongrac 2017). Most species that hyperaccumulate Cu or Co have been found in the Katangan Copperbelt (D.R. Congo), where natural Cu/Co outcrops occur, and many of these species have been shown to hyperaccumulate both Cu and Co (Lange et al. 2017). The multiple incidences of the evolution of Se hyperaccumulation among eudicots (Cappa and Pilon-Smits 2014, White 2016a), and in species within the *Astragalus* [Fabaceae] (White 2016a) and *Stanleya* [Brassicaceae] (Cappa et al. 2015) genera, have led to an explanation of the evolution of this trait, from the acquisition of tissue Se-tolerance and the colonisation of an environmental niche to the benefits of Se-hyperaccumulation in defence against herbivores, alleviation of oxidative stress and allelopathy (El Mehdawi and Pilon-Smits 2012, Schiavon and Pilon-Smits 2017).

The incidence of Al hyperaccumulation, defined as a shoot Al concentration exceeding 2.3–3.9 mg g^{-1} DM in a tropical flora and 1.1 mg g^{-1} DM in a temperate flora, is far greater among angiosperms (19% species surveyed) than hyperaccumulation of the mineral elements described above (Metali et al. 2012). Since Al hyperaccumulation is more prevalent in non-flowering plants (45% of species surveyed) than angiosperms, it has been suggested that this trait evolved early in the evolution of land plants and might be a primitive trait required for survival in ancient Al-rich environments (Jansen et al. 2002, Metali et al. 2012). There is considerable phylogenetic variation in leaf Al concentration, which occurs predominantly at the level of the family and above (Watanabe et al. 2007).

The abnormal accumulation of other elements, which is often associated with biomineralisation, has also been reported (He et al. 2014). For example, regionally dominant gypsophile species can have leaf S concentrations of 10–80 mg g^{-1} DM when growing on gypsum substrates where most non-endemic (gypsovag) species contain leaf S concentrations <1–5 mg g^{-1} DM (Ernst 1998, Escudero et al. 2015, Reid et al. 2016, Muller et al. 2017). Although this trait is likely to be most advantageous on gypsum-rich soils, the ability of plants to accumulate S by precipitating calcium or magnesium sulfate is not restricted to gypsophile species and some of their gypsovag relatives also exhibit the trait (Reid et al. 2016, Muller et al. 2017). In addition to Brassicales species, the phylogenetic inheritance of a constitutively large leaf S concentration is evident within the *Acacia* [Fabaceae], *Anulocaulis* [Nyctaginaceae, Caryphyllales] and *Tiquilia* [Boraginaceae] genera (Reid et al. 2016, Muller et al. 2017).

Recently, the hyperaccumulation of Na, defined as an abnormally large shoot Na concentration in excess of 4 mg g^{-1} DM when grown in a non-saline environment, has been reported in some Caryophyllales species (White et al. 2017). Mapping this trait onto phylogenetic relationships between Caryophyllales families, and between subfamilies within the Amaranthaceae family, indicated that this trait evolved several times within the order. It evolved in an ancestor of the Aizoaceae, but not the Phytolaccaceae or Nyctaginaceae, in ancestors of several lineages formerly classified as Chenopodiaceae, but not in the Amaranthaceae sensu stricto, and in ancestors of species within the Cactaceae,

Portulacaceae, Plumbaginaceae, Tamaricaceae and Polygonaceae (White et al. 2017).

Conclusions and perspective

Variation in the leaf ionome among plant species can have consequences for ecology, mineral cycling in the environment, strategies for the phytoremediation of contaminated land, sustainable agriculture and the nutrition of livestock and humans. In this paper, a 'standard functional leaf ionome' has been defined, which comprises the concentrations of 14 mineral nutrients in leaves of the 'average' angiosperm when plant growth is not limited by mineral nutrients. This can be used to facilitate comparisons of the effects of both environment and genetics on the leaf ionome. The environment exerts a significant effect on the leaf ionome by influencing both the growth and development of plants and the phytoavailability of mineral elements in the soil. Interactions between mineral elements occur in their uptake by roots, regulation of their concentrations in tissues and cellular compartments through non-selective transport processes, common metabolic pathways, obligate biochemical stoichiometries and their effects on electrochemical or osmotic gradients. These interactions might be characteristic of particular abiotic stresses and, therefore, the leaf ionome could have diagnostic potential for such stresses. Nevertheless, strong (phylo)genetic effects on the leaf ionome can be observed, even when plants are sampled from many contrasting environments. The evolution of differences in leaf concentrations of Mg, Ca and S, as well as the hyperaccumulation of some mineral elements, has been traced using phylogenetic relationships among angiosperm orders, families and genera. The ease of acquiring omic data sets, including ionomic data sets, from angiosperm species will facilitate greater understanding of the molecular biology, genetics, ecological significance and evolution of ionomic phenotypes in plants. This knowledge might be used to develop appropriate land management practices for enhancing biodiversity, select plants for the phytoremediation of contaminated land, or develop nutritious crops requiring less fertiliser or yielding more on marginal soils.

Author contributions

K.N., M.R.B., M.F.M. and P.J.W. compiled ionomic data. K.N., J.W.M. and P.J.W. analysed the data. All authors helped conceive the manuscript. P.J.W. and K.N. wrote the manuscript, whilst K.N., T.S.G., J.W.M. and P.J.W. developed the figures. All authors commented on the manuscript.

Acknowledgements – We thank Maria Claudia Mendes Sorreano for providing a copy of her thesis and Paula Pongrac for her comments on the original version of the manuscript. This work was supported by the Rural and Environment Science and Analytical Services Division (RESAS) of the Scottish Government, the Distinguished Scientist Fellowship Program of King Saud University, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) Brazil (Science Without Borders Project #402868/2012-9), and a University of Nottingham/James Hutton Institute Postgraduate Studentship to Konrad Neugebauer

References

Angiosperm Phylogeny Group IV [APGIV] (2016) An update of the angiosperm phylogeny group classification for the orders and families of flowering plants: APG IV. Bot J Linn Soc 181: 1–20

Baxter I (2015) Should we treat the ionome as a combination of individual elements, or should we be deriving novel combined traits? J Exp Bot 66: 2127–2131

Baxter IR, Vitek O, Lahner B, Muthukumar B, Borghi M, Morrissey J, Guerinot ML, Salt DE (2008) The leaf ionome as a multivariable system to detect a plant's physiological status. Proc Natl Acad Sci USA 105: 12081–12086

Baxter I, Hermans C, Lahner B, Yakubova E, Tikhonova M, Verbruggen N, Chao D-Y, Salt DE (2012) Biodiversity of mineral nutrient and trace element accumulation in *Arabidopsis thaliana*. PLoS One 7: e35121

Beresford NA, Broadley MR, Howard BJ, Barnett CL, White PJ (2004) Estimating radionuclide transfer to wild species – data requirements and availability for terrestrial ecosystems. J Radiol Prot 24: A89–A103

Broadley MR, White PJ (2012) Some elements are more equal than others: soil-to-plant transfer of radiocaesium and radiostrontium, revisited. Plant Soil 355: 23–27

Broadley MR, Willey NJ, Wilkins JC, Baker AJM, Mead A, White PJ (2001) Phylogenetic variation in heavy metal accumulation in angiosperms. New Phytol 152: 9–27

Broadley MR, Bowen HC, Cotterill HL, Hammond JP, Meacham MC, Mead A, White PJ (2003) Variation in the shoot calcium content of angiosperms. J Exp Bot 54: 1431–1446

Broadley MR, Bowen HC, Cotterill HL, Hammond JP, Meacham MC, Mead A, White PJ (2004) Phylogenetic variation in the shoot mineral concentration of angiosperms. J Exp Bot 55: 321–336

Broadley MR, White PJ, Hammond JP, Zelko I, Lux A (2007) Zinc in plants. New Phytol 173: 677–702

Broadley M, Brown P, Cakmak I, Rengel Z, Zhao F (2012a) Function of nutrients: Micronutrients. In: Marschner P (ed) Marschner's Mineral Nutrition of Higher Plants, 3rd Edn. Academic Press, London, pp 191–248

Broadley M, Brown P, Cakmak I, Ma JF, Rengel Z, Zhao F (2012b) Beneficial elements. In: Marschner P (ed) Marschner's Mineral Nutrition of Higher Plants, 3rd Edn. Academic Press, London, pp 249–269

Brooker RW, Bennett AE, Cong W-F, Daniell TJ, George TS, Hallett PD, Hawes C, Ianetta PPM, Jones HG, Karley AJ, Li L, McKenzie BM, Pakeman RJ, Paterson E, Schöb C, Shen J, Squire G, Watson CA, Zhang C, Zhang F, Zhang J, White PJ (2015) Improving intercropping: a synthesis of research in agronomy, plant physiology and ecology. New Phytol 206: 107–117

Brown LK, George TS, Neugebauer K, White PJ (2017) The rhizosheath – a potential trait for future agricultural sustainability occurs in orders throughout the angiosperms. Plant Soil 418: 115–128

Cakmak I, Pfeiffer WH, McClafferty B (2010) Biofortification of durum wheat with zinc and iron. Cereal Chem 87: 10–20

Campos ACAL, Kruijer W, Alexander R, Akkers RC, Danku J, Salt DE, Aarts MGM (2017) Natural variation in *Arabidopsis thaliana* reveals shoot ionome, biomass, and gene expression changes as biomarkers for zinc deficiency tolerance. J Exp Bot 68: 3643–3656

Cappa JJ, Pilon-Smits EAH (2014) Evolutionary aspects of elemental hyperaccumulation. Planta 239: 267–275

Cappa JJ, Yetter C, Fakra S, Cappa PJ, DeTar R, Landes C, Pilon-Smits EA, Simmons MP (2015) Evolution of selenium hyperaccumulation in *Stanleya* (Brassicaceae) as inferred from phylogeny, physiology and X-ray microprobe analysis. New Phytol 205: 583–595

Carnicer J, Sardans J, Stefanescu C, Ubach A, Bartrons M, Asensio D, Peñuelas J (2015) Global biodiversity, stoichiometry and ecosystem function responses to human-induced C-N-P imbalances. J Plant Physiol 172: 82–91

Conn S, Gilliham M (2010) Comparative physiology of elemental distributions in plants. Ann Bot 105: 1081–1102

Cornwell WK, Westoby M, Falster DS, FitzJohn RG, Meara BCO, Pennell MW, McGlinn DJ, Eastman JM, Moles AT, Reich PB, Tank DC, Wright IJ, Aarssen L, Beaulieu JM, Kooyman RM, Leishman MR, Miller ET, Niinemets U, Oleksyn J, Ordonez A, Royer DL, Smith SA, Stevens PF, Warman L, Wilf P, Zanne AE (2014) Functional distinctiveness of major plant lineages. J Ecol 102: 345–356

Crawley MJ, Johnston AE, Silvertown J, Dodd M, de Mazancourt C, Heard MS, Henman DF, Edwards GR (2005) Determinants of species richness in the Park Grass experiment. Am Nat 165: 179–192

Delhaize E, Ma JF, Ryan PR (2012) Transcriptional regulation of aluminium tolerance genes. Trends Plant Sci 17: 341–348

Department for Environment, Food and Rural Affairs [Defra] (2010) Fertiliser Manual (RB209), 8th Edn. The Stationery Office, Norwich

Dhillon KS, Bañuelos GS (2017) Overview and prospects of selenium phytoremediation approaches. In: Pilon-Smits EAH, Winkel LHE, Lin Z-Q (eds) Selenium in Plants: Molecular, Physiological, Ecological and Evolutionary Aspects. Springer, Cham, pp 277–321

Dove H, Masters DG, Thompson AN (2016) New perspectives on the mineral nutrition of livestock grazing cereal and canola crops. Anim Prod Sci 56: 1350–1360

Eggert K, von Wirén N (2013) Dynamics and partitioning of the ionome in seeds and germinating seedlings of winter oilseed rape. Metallomics 5: 1316–1325

El Mehdawi AF, Pilon-Smits EAH (2012) Ecological aspects of plant selenium hyperaccumulation. Plant Biol 14: 1–10

Elser JJ, Fagan WF, Kerkhoff AJ, Swenson NG, Enquist BJ (2010) Biological stoichiometry of plant production: metabolism, scaling and ecological response to global change. New Phytol 186: 593–608

Ernst WHO (1998) Sulfur metabolism in higher plants: potential for phytoremediation. Biodegradation 9: 311–318

Escudero A, Palacio S, Maestre FT, Luzuriaga AL (2015) Plant life on gypsum: a review of its multiple facets. Biol Rev 90: 1–18

Fageria NK (2009) The Use of Nutrients in Crop Plants. CRC Press, Boca Raton

Fageria NK, Baligar VC, Jones CA (2011) Growth and Mineral Nutrition of Field Crops. CRC Press, Boca Raton

Flowers TJ, Munns R, Colmer TD (2015) Sodium chloride toxicity and the cellular basis of salt tolerance in halophytes. Ann Bot 115: 419–431

de la Fuente V, Rufo L, Rodríguez N, Franco A, Amils R (2017) Comparison of iron localization in wild plants and hydroponic cultures of *Imperata cylindrica* (L.) P. Beauv. Plant Soil 418: 25–35

Fyllas NM, Patino S, Baker TR, Bielefeld Nardoto G, Martinelli LA, Quesada CA, Paiva R, Schwarz M, Horna V, Mercado LM, Santos A, Arroyo L, Jimenez EM, Luizão FJ, Neill DA, Silva N, Prieto A, Rudas A, Silviera M, Vieira ICG, Lopez-Gonzalez G, Malhi Y, Phillips OL, Lloyd J (2009) Basin-wide variations in foliar properties of Amazonian forest: phylogeny, soils and climate. Biogeosciences 6: 2677–2708

Garten CT (1976) Correlations between concentrations of elements in plants. Nature 261: 686–688

Garten CT (1978) Multivariate perspectives on ecology of plant mineral element composition. Am Nat 112: 533–544

Greenway H, Munns R (1980) Mechanisms of salt tolerance in nonhalophytes. Annu Rev Plant Physiol 31: 149–190

Greenwood DJ, Barnes A, Liu K, Hunt J, Cleaver TJ, Loquens SMH (1980) Relationships between the critical concentrations of nitrogen, phosphorus and potassium in 17 different vegetable crops and duration of growth. J Sci Food Agric 31: 1343–1353
Grime JP (2001) Plant Strategies, Vegetation Processes, and Ecosystem Properties, 2nd Edn. Wiley, Chichester
Grime JP, Pierce S (2012) The Evolutionary Strategies that Shape Ecosystems. John Wiley & Sons, Chichester
Grusak MA, Broadley MR, White PJ (2016) Plant macro- and micro-nutrient minerals. In: eLS. John Wiley & Sons, Chichester Available at http://www.els.net (accessed 8 October 2017)
Güsewell S (2004) N : P ratios in terrestrial plants: variation and functional significance. New Phytol 164: 243–266
Hao Z, Kuang Y, Kang M (2014) Untangling the influence of phylogeny, soil and climate on leaf element concentrations in a biodiversity hotspot. Funct Ecol 29: 165–176
Hawkesford M, Horst W, Kichey T, Lambers H, Schjoerring J, Skrumsager Møller I, White P (2012) Functions of macronutrients. In: Marschner P (ed) Marschner's Mineral Nutrition of Higher Plants, 3rd Edn. Academic Press, London, pp 135–189
Hayes P, Turner BL, Lambers H, Laliberté E (2014) Foliar nutrient concentrations and resorption efficiency in plants of contrasting nutrient-acquisition strategies along a 2-million-year dune chronosequence. J Ecol 102: 396–410
He H, Veneklaas EJ, Kuo J, Lambers H (2014) Physiological and ecological significance of biomineralization in plants. Trends Plant Sci 19: 166–174
He M, Dijkstra FA, Zhang K, Tan H, Zhao Y, Li X (2016) Influence of life form, taxonomy, climate, and soil properties on shoot and root concentrations of 11 elements in herbaceous plants in a temperate desert. Plant Soil 398: 339–350
Hejcman M, Češková M, Schellberg J, Pätzold S (2010) The Rengen grassland experiment: effect of soil chemical properties on biomass production, plant species composition and species richness. Folia Geobot 45: 125–142
Hejcman M, Sochorová L, Pavlů V, Štrobach J, Diepolder M, Schellberg J (2014) The Steinach grassland experiment: soil chemical properties, sward height and plant species composition in three cut alluvial meadow after decades-long fertilizer application. Agric Ecosyst Environ 184: 76–87
Hermans C, Hammond JP, White PJ, Verbruggen N (2006) How do plants respond to nutrient shortage by biomass allocation? Trends Plant Sci 11: 610–617
Hodson MJ, White PJ, Mead A, Broadley MR (2005) Phylogenetic variation in the silicon composition of plants. Ann Bot 96: 1027–1046
Jansen S, Broadley MR, Robbrecht E, Smets E (2002) Aluminium hyperaccumulation in angiosperms: a review of its phylogenetic significance. Bot Rev 68: 235–269
Jin K, White PJ, Whalley WR, Shen J, Shi L (2017) Shaping an optimal soil by root-soil interaction. Trends Plant Sci 22: 823–829
Kerkhoff AJ, Fagan WF, Elser JJ, Enquist BJ (2006) Phylogenetic and growth form variation in the scaling of nitrogen and phosphorus in the seed plants. Am Nat 168: E103–E122
Kidd J, Manning P, Simkin J, Peacock S, Stockdale E (2017) Impacts of 120 years of fertilizer addition on a temperate grassland ecosystem. PLoS One 12: e0174632
Knowles SO, Grace ND (2013) A recent assessment of the elemental composition of New Zealand pastures in relation to meeting the dietary requirements of grazing livestock. J Anim Sci 92: 303–310
Koch MA, German DA (2013) Taxonomy and systematics are key to biological information: *Arabidopsis*, *Eutrema* (*Thellungiella*), *Noccaea* and *Schrenkiella* (Brassicaceae) as examples. Front Plant Sci 4: 267
Koerselman W, Meuleman AFM (1996) The vegetation N:P ratio: a new tool to detect the nature of nutrient limitation. J Appl Ecol 33: 1441–1450
Krämer U (2010) Metal hyperaccumulation in plants. Annu Rev Plant Biol 61: 517–534
Kumar S, Stecher G, Suleski M, Hedges SB (2017) TimeTree: a resource for timelines, timetrees, and divergence times. Mol Biol Evol 34: 1812–1819
Lambers H, Finnegan PM, Jost R, Plaxton WC, Shane MW, Stitt M (2015) Phosphorus nutrition in Proteaceae and beyond. Nat Plants 1: 15109
Lange B, van der Ent A, Baker AJM, Echevarria G, Mahy G, Malaisse F, Meerts P, Pourret O, Verbruggen N, Faucon M-P (2017) Copper and cobalt accumulation in plants: a critical assessment of the current state of knowledge. New Phytol 213: 537–551
Maillard A, Etienne P, Diquélou S, Trouverie J, Billard V, Yvin J-C, Ourry A (2016) Nutrient deficiencies modify the ionomic composition of plant tissues: a focus on cross-talk between molybdenum and other nutrients in *Brassica napus*. J Exp Bot 67: 5631–5641
Metali F, Salim KA, Burslem DFRP (2012) Evidence of foliar aluminium accumulation in local, regional and global datasets of wild plants. New Phytol 193: 637–649
Mueller ND, Gerber JS, Johnston M, Ray DK, Ramankutty N, Foley JA (2012) Closing yield gaps through nutrient and water management. Nature 490: 254–257
Muller CT, Moore MJ, Feder Z, Tiley H, Drenovsky RE (2017) Phylogenetic patterns of foliar mineral nutrient accumulation among gypsophiles and their relatives in the Chihuahuan Desert. Am J Bot 104: 1442–1450

Niklas KJ (2006) Plant allometry, leaf nitrogen and phosphorus stoichiometry, and interspecific trends in annual growth rates. Ann Bot 97: 155–163

Oliveira RS, Galvão HC, de Campos MCR, Eller CB, Pearse SJ, Lambers H (2015) Mineral nutrition of *Campos rupestres* plant species on contrasting nutrient-impoverished soil types. New Phytol 205: 1183–1194

Olsen CE, Huang X-C, Hansen CIC, Cipollini D, Ørgaard M, Matthes A, Geu-Flores F, Koch MA, Agerbirk N (2016) Glucosinolate diversity within a phylogenetic framework of the tribe Cardamineae (Brassicaceae) unraveled with HPLC-MS/MS and NMR-based analytical distinction of 70 desulfoglucosinolates. Phytochemistry 132: 33–56

Osaki M, Yamada S, Ishizawa T, Watanabe T, Shinano T, Tuah SJ, Urayama M (2003) Mineral characteristics of leaves of plants from different phylogeny grown in various soil types in the temperate region. Plant Foods Hum Nutr 58: 117–137

Ostertag R, DiManno NM (2016) Detecting terrestrial nutrient limitation: a global meta-analysis of foliar nutrient concentrations after fertilization. Front Earth Sci 4: 23

Parent SE, Parent LE, Egozcue JJ, Rozane D-E, Hernandes A, Lapointe L, Hébert-Gentile V, Naess K, Marchand S, Lafond J, Mattos D Jr, Barlow P, Natale W (2013a) The plant ionome revisited by the nutrient balance concept. Front Plant Sci 4: 39

Parent SE, Parent LE, Rozane DE, Natale W (2013b) Plant ionome diagnosis using sound balances: case study with mango (*Mangifera indica*). Front Plant Sci 4: 449

Penrose B, Johnson KA, Arkhipov A, Maksimenko A, Gaschak S, Meacham MC, Crout NJM, White PJ, Beresford NA, Broadley MR (2016) Inter-cultivar variation in soil-to-plant transfer of radiocaesium and radiostrontium in *Brassica oleracea*. J Environ Radioact 155-156: 112–121

Persson DP, Chen A, Aarts MGM, Salt DE, Schjoerring JK, Husted S (2016) Multi-element bioimaging of *Arabidopsis thaliana* roots. Plant Physiol 172: 835–847

Pii Y, Cesco S, Mimmo T (2015) Shoot ionome to predict the synergism and antagonism between nutrients as affected by substrate and physiological status. Plant Physiol Biochem 94: 48–56

Quintero-Vallejo E, Peña-Claros M, Bongers F, Toledo M, Poorter L (2015) Effects of Amazonian dark earths on growth and leaf nutrient balance of tropical tree seedlings. Plant Soil 396: 241–255

Raven JA (2015) Interactions between nitrogen and phosphorus metabolism. Annu Plant Rev 48: 187–214

Reeves RD (2006) Hyperaccumulation of trace elements by plants. In: Morel J-L, Echevarria G, Goncharova N (eds) Phytoremediation of Metal-Contaminated Soils. Springer, Berlin, pp 25–52

Reich PB, Oleksyn J (2004) Global patterns of plant leaf N and P in relation to temperature and latitude. Proc Natl Acad Sci USA 101: 11001–11006

Reich PB, Oleksyn J, Wright IJ, Niklas KJ, Hedin L, Elser JJ (2010) Evidence of a general 2/3-power law of scaling leaf nitrogen to phosphorus among major plant groups and biomes. Proc R Soc B 277: 877–883

Reid N, Robson TC, Radcliffe B, Verrall M (2016) Excessive sulphur accumulation and ionic storage behaviour identified in species of *Acacia* (Leguminosae: Mimosoideae). Ann Bot 117: 653–666

Ronse de Craene LP, Haston E (2006) The systematic relationships of glucosinolate-producing plants and related families: a cladistic investigation based on morphological and molecular characters. Bot J Linn Soc 151: 453–494

Rozema J, Schat H (2013) Salt tolerance of halophytes, research questions reviewed in the perspective of saline agriculture. Environ Exp Bot 92: 83–95

Salt DE, Baxter I, Lahner B (2008) Ionomics and the study of the plant ionome. Annu Rev Plant Biol 59: 709–733

Saltzman A, Birol E, Bouis HE, Boy E, De Moura FF, Islam Y, Pfeiffer WH (2013) Biofortification: progress toward a more nourishing future. Glob Food Sec 2: 9–17

Sánchez-Rodríguez E, del Mar Rubio-Wilhelmi M, Cervilla LM, Blasco B, Rios JJ, Leyva R, Romero L, Ruiz JM (2010) Study of the ionome and uptake fluxes in cherry tomato plants under moderate water stress conditions. Plant Soil 335: 339–347

Sardans J, Janssens IA, Alonso R, Veresoglou SD, Rillig MC, Sanders TGM, Carnicer J, Filella I, Farré-Armengol G, Peñuelas J (2015) Foliar elemental composition of European forest tree species associated with evolutionary traits and present environmental and competitive conditions. Glob Ecol Biogeogr 24: 240–255

Saslis-Lagoudakis CH, Moray L, Bromham L (2014) Evolution of salt tolerance in angiosperms: A phylogenetic approach. In: Rajakaruna N, Boyd RS, Harris TB (eds) Plant Ecology and Evolution in Harsh Environments. Nova Science, Hauppauge, pp 77–95

Schiavon M, Pilon-Smits EAH (2017) The fascinating facets of plant selenium accumulation - biochemistry, physiology, evolution and ecology. New Phytol 213: 1582–1596

Schonewille JT (2013) Magnesium in dairy cow nutrition: an overview. Plant Soil 368: 167–178

Semelova V, Hejcman M, Pavlu V, Vacek S, Podrazsky V (2008) The grass garden in the Giant Mts. (Czech Republic): residual effect of long-term fertilization after 62 years. Agric Ecosyst Environ 123: 337–342

Sorreano MCM (2006) Avaliação da exigencia nutricional na fase inicial do crescimento de espécies florestais nativas. Universidade de São Paulo, Piracicaba, Tese Doutorado

Sterckeman T, Cazes Y, Gonneau C, Sirguey C (2017) Phenotyping 60 populations of *Noccaea caerulescens* provides a broader knowledge of variation in traits of interest for phytoextraction. Plant Soil 418: 523–540
Sterner RW, Elser JJ (2002) Ecological Stoichiometry. The Biology of Elements from Molecules to the Biosphere. Princeton University Press, Princeton
Stevens PF (2001) Angiosperm phylogeny website. Version 14. Available at http://www.mobot.org/MOBOT/research/APweb/ (accessed 22 April 2017)
Subramanian NK, White PJ, Broadley MR, Ramsay G (2011) The three-dimensional distribution of minerals in potato tubers. Ann Bot 107: 681–691
Thomas CL, Alcock TD, Graham NS, Hayden R, Matterson S, Wilson L, Young SD, Dupuy LX, White PJ, Hammond JP, Danku JMC, Salt DE, Sweeney A, Bancroft I, Broadley MR (2016) Root morphology and seed and leaf ionomic traits in a *Brassica napus* L. diversity panel show wide phenotypic variation and are characteristic of crop habit. BMC Plant Biol 16: 214
Thompson K, Parkinson JA, Band SR, Spencer RE (1997) A comparative study of leaf nutrient concentrations in a regional herbaceous flora. New Phytol 136: 679–689
Tomasi N, Mimmo T, Terzano R, Alfeld M, Janssens K, Zanin L, Pinton R, Varanini Z, Cesco S (2014) Nutrient accumulation in leaves of Fe-deficient cucumber plants treated with natural Fe complexes. Biol Fertil Soils 50: 973–982
Van der Ent A, Baker AJM, Reeves RD, Pollard AJ, Schat H (2013) Hyperaccumulators of metal and metalloid trace elements: facts and fiction. Plant Soil 362: 319–334
Veneklaas EJ, Lambers H, Bragg J, Finnegan PM, Lovelock CE, Plaxton WC, Price CA, Scheible W-R, Shane MW, White PJ, Raven JA (2012) Opportunities for improving phosphorus-use efficiency in crop plants. New Phytol 195: 306–320
Verboom GA, Stock WD, Cramer MD (2017) Specialization to extremely low-nutrient soils limits the nutritional adaptability of plant lineages. Am Nat 189: 684–699
Viani RAG, Rodrigues RR, Dawson TE, Oliveira RS (2011) Savanna soil fertility limits growth but not survival of tropical forest tree seedlings. Plant Soil 349: 341–353
Viani RAG, Rodrigues RR, Dawson TE, Lambers H, Oliveira RS (2014) Soil pH accounts for differences in species distribution and leaf nutrient concentrations of Brazilian woodland savannah and seasonally dry forest species. Perspect Plant Ecol Evol Syst 16: 64–74
Watanabe T, Broadley MR, Jansen S, White PJ, Takada J, Satake K, Takamatsu T, Tuah SJ, Osaki M (2007) Evolutionary control of leaf element composition in plants. New Phytol 174: 516–523
Watanabe T, Urayama M, Shinano T, Okada R, Osaki M (2015) Application of ionomics to plant and soil in fields under long-term fertilizer trials. SpringerPlus 4: 781
Watanabe T, Maejima E, Yoshimura T, Urayama M, Yamauchi A, Owadano M, Okada R, Osaki M, Kanayama Y, Shinano T (2016) The ionomic study of vegetable crops. PLoS One 11: e0160273
Watson CA, Öborn I, Edwards AC, Dahlin AS, Eriksson J, Lindström BEM, Linse L, Owensa K, Topp CFE, Walker RL (2012) Using soil and plant properties and farm management practices to improve the micronutrient composition of food and feed. J Geochem Explor 121: 15–24
White PJ (2001) The pathways of calcium movement to the xylem. J Exp Bot 52: 891–899
White PJ (2012) Ion uptake mechanisms of individual cells and roots: Short-distance transport. In: Marschner P (ed) Marschner's Mineral Nutrition of Higher Plants, 3rd Edn. Academic Press, London, pp 7–47
White PJ (2013) Improving potassium acquisition and utilisation by crop plants. J Plant Nutr Soil Sci 176: 305–316
White PJ (2016a) Selenium accumulation by plants. Ann Bot 117: 217–235
White PJ (2016b) Biofortification of edible crops. In: eLS. John Wiley & Sons, Chichester Available at http://www.els.net (accessed 8 October 2017)
White PJ, Broadley MR (2003) Calcium in plants. Ann Bot 92: 487–511
White PJ, Broadley MR (2009) Biofortification of crops with seven mineral elements often lacking in human diets – iron, zinc, copper, calcium, magnesium, selenium and iodine. New Phytol 182: 49–84
White PJ, Brown PH (2010) Plant nutrition for sustainable development and global health. Ann Bot 105: 1073–1080
White PJ, Pongrac P (2017) Heavy metal toxicity in plants. In: Shabala S (ed) Plant Stress Physiology, 2nd Edn. CABI, Wallingford, pp 301–332
White PJ, Swarup K, Escobar-Gutiérrez AJ, Bowen HC, Willey NJ, Broadley MR (2003) Selecting plants to minimise radiocaesium in the food chain. Plant Soil 249: 177–186
White PJ, Bowen HC, Marshall B, Broadley MR (2007) Extraordinarily high leaf selenium to sulphur ratios define 'Se-accumulator' plants. Ann Bot 100: 111–118
White PJ, Broadley MR, Gregory PJ (2012a) Managing the nutrition of plants and people. Appl Environ Soil Sci 2012: 104826
White PJ, Broadley MR, Thompson JA, McNicol JW, Crawley MJ, Poulton PR, Johnston AE (2012b) Testing the distinctness of shoot ionomes of angiosperm families using the Rothamsted Park Grass Continuous Hay Experiment. New Phytol 196: 101–109
White PJ, George TS, Dupuy LX, Karley AJ, Valentine TA, Wiesel L, Wishart J (2013a) Root traits for infertile soils. Front Plant Sci 4: 193

White PJ, George TS, Gregory PJ, Bengough AG, Hallett PD, McKenzie BM (2013b) Matching roots to their environment. Ann Bot 112: 207–222
White PJ, Bowen HC, Farley E, Shaw EK, Thompson JA, Wright G, Broadley MR (2015) Phylogenetic effects on shoot magnesium concentration. Crop Pasture Sci 66: 1241–1248
White PJ, Bowen HC, Broadley MR, El-Serehy HA, Neugebauer K, Taylor A, Thompson JA, Wright G (2017) Evolutionary origins of abnormally large shoot sodium accumulation in nonsaline environments within the Caryophyllales. New Phytol 214: 284–293
White PJ, Broadley MR, El-Serehy HA, George TS, Neugebauer K (2018) A hypothesis to explain linear relationships between shoot magnesium and calcium concentrations among angiosperm species based on cell wall chemistry. Ann Bot, submitted
Willby NJ, Pulford ID, Flowers TH (2001) Tissue nutrient signatures predict herbaceous-wetland community responses to nutrient availability. New Phytol 152: 463–481
Willey NJ (2014) Soil to plant transfer of radionuclides: predicting the fate of multiple radioisotopes in plants. J Environ Radioact 133: 31–34
Willey N, Fawcett K (2005) Species selection for phytoremediation of $^{36}Cl/^{35}Cl$ using angiosperm phylogeny and inter-taxa differences in uptake. Int J Phytoremediation 7: 295–306
Willey N, Wilkins J (2006) An analysis of intertaxa differences in sulfur concentration in angiosperms. J Plant Nutr Soil Sci 169: 717–727
Wright IJ, Reich PB, Westoby M, Ackerly DD, Baruch Z, Bongers F, Cavender-Bares J, Chapin T, Cornelissen JHC, Diemer M, Flexas J, Garnier E, Groom PK, Gulias J, Hikosaka K, Lamont BB, Lee T, Lee W, Lusk C, Midgley JJ, Navas M-L, Niinemets Ü, Oleksyn J, Osada N, Poorter H, Poot P, Prior L, Pyankov VI, Roumet C, Thomas SC, Tjoelker MG, Veneklaas EJ, Villar R (2004) The world-wide leaf economics spectrum. Nature 428: 821–827
Yang C, Zheng S, Huang H, Liu Z, Zheng W, Liu B, Shi D (2012) Comparison of osmotic adjustment and ion balance strategies in nineteen alkali-tolerant halophyte species during adaptation to salt-alkalinized habitats in northeast China. Aust J Crop Sci 6: 141–148
Zhang S-B, Zhang J-L, Slik JWF, Cao K-F (2012) Leaf element concentrations of terrestrial plants across China are influenced by taxonomy and the environment. Glob Ecol Biogeogr 21: 809–818
Zhao F-J, Moore KL, Lombi E, Zhu Y-G (2014) Imaging element distribution and speciation in plant cells. Trends Plant Sci 19: 183–192

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Mean concentrations of nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), chlorine (Cl), boron (B), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), sodium (Na) and organic-N (organic N).

Edited by J. K. Schjørring